Supporting Information

A Useful Valence-alterable Optical Probe to Serve the Predict of Material Characteristics Based on Theoretical Calculation

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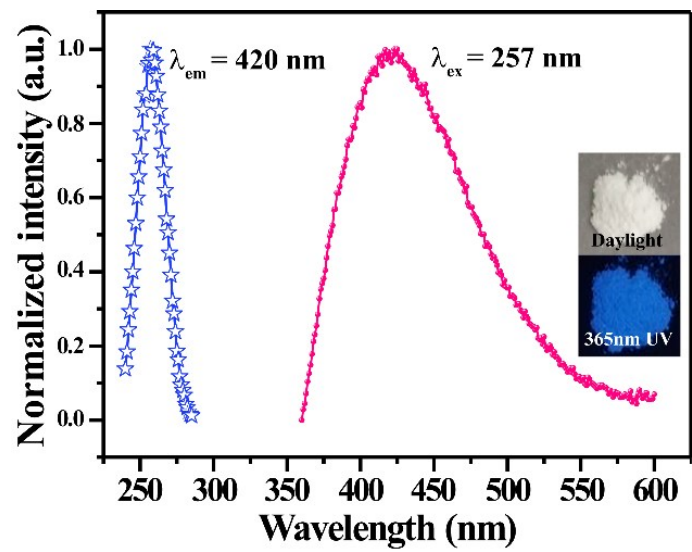[§]Both authors contributed equally to this work.

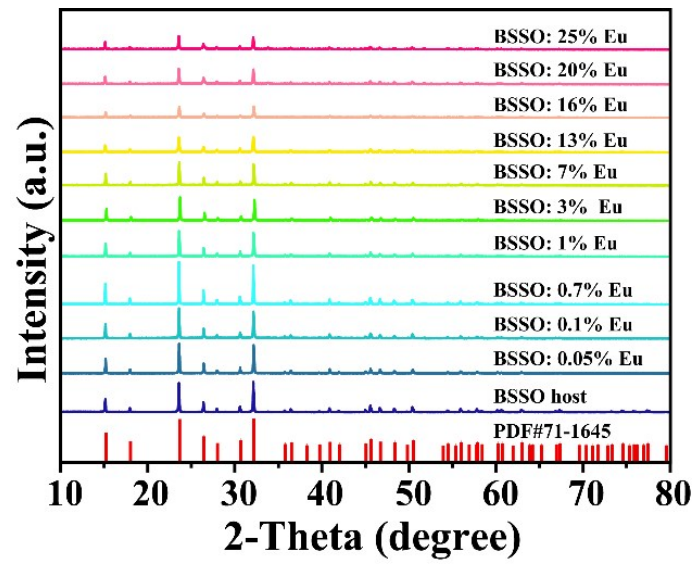**Figure S1.** The PLE spectrum (λ_{em}=422 nm) and PL spectrum (λ_{ex}=257 nm) of BSSO host.

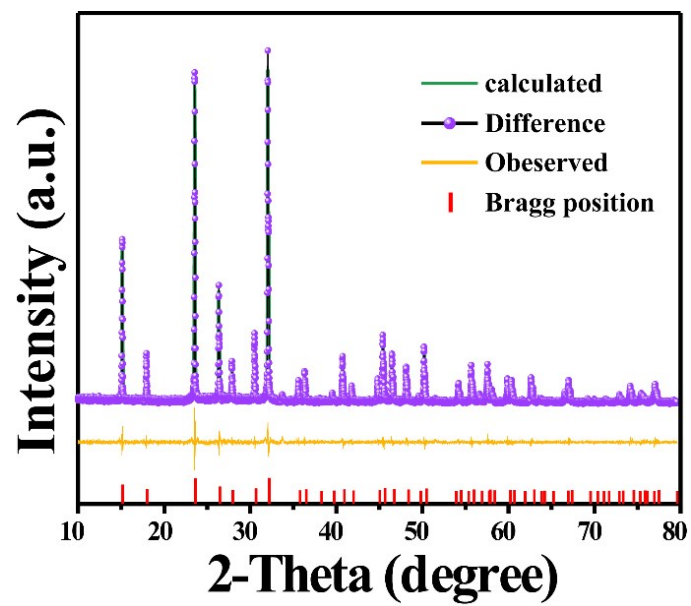**Figure S2.** The XRD patterns of the samples BSSO:X % Eu (X=0-25).

Figure S3. The Rietveld refinement XRD pattern of the typical sample $BaSnSi_3O_9$:13% Eu.
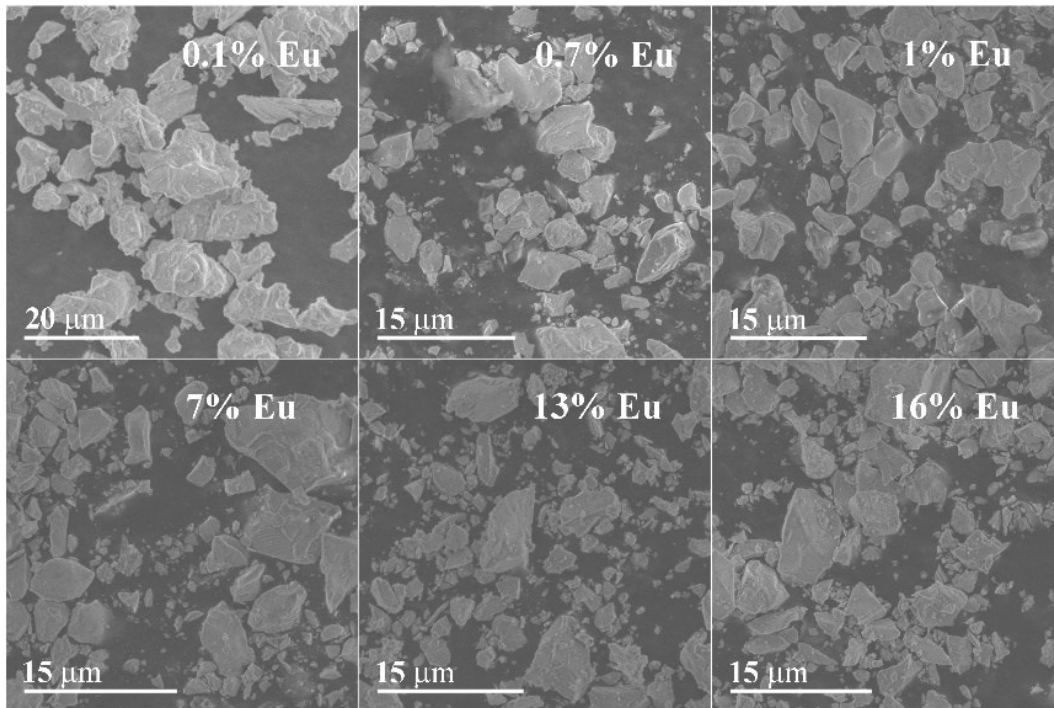
Figure S4. The SEM images of BSSO:X% Eu (X= 0.1, 0.7, 1, 7, 13, 16).

The mic-morphologies of the typical samples $BaSnSi_3O_9$:X% Eu mainly present the uneven and micro-scale blocks in **Figure S4**.
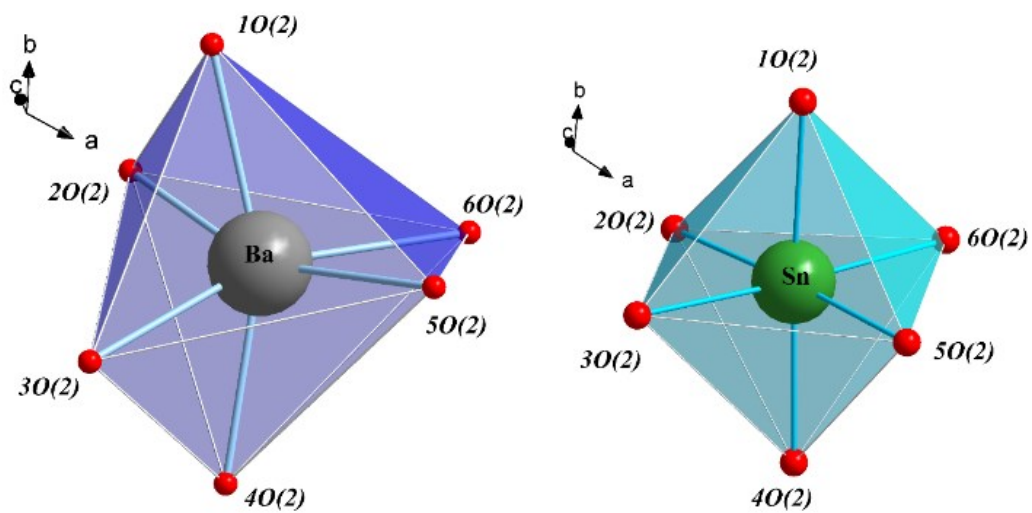
Figure S5. The spatial three-dimensional BaO$_6$ and SnO$_6$ octahedral structure of matrix BSSO.

Table S1. The *a*, *b* and *c* values of crystal structure BSSO after the CASTEP *GeomOpt* .

Unit Cell					
Real Lattice (Å)			**Reciprocal Lattice (1/Å)**		
5.9367671	-3.4275941	0.0000000	1.0583513	0.0000000	0.0000000
0.0000000	6.8551882	0.0000000	0.5291757	0.9165591	0.0000000
0.0000000	0.0000000	10.0341159	0.0000000	0.0000000	0.6261823
Lattice parameters (Å)			**Cell Angles**		
a=6.855188			*Alpha*=90.000000		
b=6.855188			*Beta*=90.000000		
c=10.034116			*Gamma*=120.000000		
Current cell volume=408.364996 (Å^3)					

Table S2. The detailed crystallographic parameters of BSSO obtained by Rietveld refinement of the XRD data.

Formula	$BaSnSi_3O_9$				
Crystal system	Hexagonal				
Space group lattice constants	P6-c2 (188)				
a/Å	6.7165				
b/Å	6.7165				
c/Å	9.8194				
c/a	1.46198				
α/°	90				
β/°	90				
γ/°	120				
Cell volume (V/Å^3)	383.625				
R values	R_{wp}=14.08 %				
	R_p=10.29 %				
χ^2	1.937				
Atom	**Wyck**	**x/a**	**y/b**	**z/c**	
Ba	2e	0.6667	0.3333	0	
Sn	2c	0.3333	0.6667	0	
Si	6k	0.0645	0.2854	0.2500	
O1	6k	0.2398	0.1835	0.2500	
O2	12l	0.0805	0.4227	0.1167	
Bond	**Length(Å)**	**Bond**	**Length(Å)**	**Bond**	**Length(Å)**
Ba-2O2	2.78027	Sn-2O2	2.02451	Si -O1	1.60613
Ba-2O2	2.78047	Sn-2O2	2.02477	Si -O1	1.63113
Ba-2O2	2.78087	Sn-2O2	2.02506	Si -2O2	1.57327

The relative deviations of ionic radius (Dr) between matrix cations and Eu^{3+}/Eu^{2+} can be calculated by following equation:[1]

$$Dr(\%) = 100 \times [R_m(CN) - R_d(CN)]/R_m(CN) \qquad (1)$$

Where Dr presents the ionic radius percentage difference; $R_m(CN)$ and $R_d(CN)$) are the radius of the host cation and the doped ion, respectively; and CN is the coordination number. The detailed radii values and the calculated Dr results of between Eu^{2+}/Eu^{3+} and Ba^{2+}, Sn^{4+}, Si^{4+} ions are shown in **Table S3**.

Table S3. The relative deviations of ionic radius between matrix cations and doping ions.[2]

Ions	Radius/Å	CN	Dr (%)
Eu^{3+}	1.087	6	0
Ba^{2+}	1.49	6	27.05
Sn^{4+}	0.830	6	-30.96
Si^{4+}	0.40	4	-171.75
Eu^{2+}	1.31	6	0
Ba^{2+}	1.49	6	12.08
Sn^{4+}	0.830	6	-57.83
Si^{4+}	0.40	4	-227.5

Table S4. The detailed crystallographic parameters of BSSO:13% Eu obtained by Rietveld refinement of the XRD data.

Formula	BaSnSi$_3$O$_9$:13% Eu				
Crystal system	Hexagonal				
Space group lattice constants	P6-c2 (188)				
a/ Å	6.7630				
b/Å	6.7630				
c/Å	9.8895				
c/a	1.4623				
α/°	90				
β/°	90				
γ/°	120				
Cell volume (V/Å^3)	391.723				
R values	R_{wp}=14.22 %				
	R_p=10.79 %				
χ^2	1.286				
Atom	**Wyck**	**x/a**	**y/b**	**z/c**	
Ba	2e	0.6667	0.3333	0	
Sn	2c	0.3333	0.6667	0	
Si	6k	0.0627	0.2851	0.2500	
O1	6k	0.2421	0.1789	0.2500	
O2	12l	0.0819	0.4206	0.1179	
Bond	**Length(Å)**	**Bond**	**Length(Å)**	**Bond**	**Length(Å)**
Ba-2O2	2.81695	Sn-2O2	2.04292	Si-O1	1.57192
Ba-2O2	2.81714	Sn-2O2	2.04719	Si-O1	1.69064
Ba-2O2	2.81755	Sn-2O2	2.04748	Si-2O2	1.56323

Table S5. The detailed information about *atom 1(O2)-Ba- atom 3(O2)* bond angle, atom 1 and atom 3 represent O2 atoms located in different position around Ba atom.

Angle	Degrees	Angle	Degrees
1O(2)-Ba-2O(2)	60.063	*1O(2)-Sn-2O(2)*	91.009
1O(2)-Ba-3O(2)	104.187	*1O(2)-Sn-3O(2)*	91.126
1O(2)-Ba-4O(2)	158.451	*1O(2)-Sn-4O(2)*	177.082
1O(2)-Ba-5O(2)	104.192	*1O(2)-Sn-5O(2)*	91.118
1O(2)-Ba-6O(2)	94.488	*1O(2-Sn-6O(2)*	86.851
4O(2)-Ba-2O(2)	104.192	*4O(2)-Sn-2O(2)*	91.118
4O(2)-Ba-3O(2)	60.075	*4O(2)-Sn-3O(2)*	90.985
4O(2)-Ba-5O(2)	94.506	*4O(2)-Sn-5O(2)*	86.826
4O(2)-Ba-6O(2)	104.203	*4O(2)-Sn-6O(2)*	91.110
2O(2)-Ba-3O(2)	94.488	*2O(2)-Sn-3O(2)*	86.851
2O(2)-Ba-5O(2)	158.451	*2O(2)-Sn-5O(2)*	177.082
2O(2)-Ba-6O(2)	104.187	*2O(2)-Sn-6O(2)*	91.126
3O(2)-Ba-5O(2)	104.203	*3O(2)-Sn-5O(2)*	91.110
3O(2)-Ba-6O(2)	158.475	*3O(2)-Sn-6O(2)*	177.115
5O(2)-Ba-6O(2)	60.075	*5O(2)-Sn-6O(2)*	90.985

Zhang and Levine[3, 4] extended the theory on the basis of the theory developed by Phillips and Van Vechten (PV),[5, 6] which is suitable to the compounds with a complex structure. In this theory, the complicated crystals with molecular formula: $A_{a1}^1 A_{a2}^2 ... A_{ai}^i B_{b1}^1 B_{b2}^2 ... B_{bj}^j$ can be expressed by the following sub-formula:

$$\frac{N(B^j - A^i) \times a^i}{N_{CA^i}} A^i \frac{N(A^i - B^j) \times b^j}{N_{CB^j}} B^j = A_{m_i}^i B_{n_j}^j \qquad (2)$$

Where

$$m_i = \frac{N(B^j - A^i) \times a^i}{N_{CA^i}} \quad n_j = \frac{N(A^i - B^j) \times b^j}{N_{CB^j}} \qquad (3)$$

The bond sub formula equation is given by

$$A_{a1}^1 A_{a2}^2 ...... A_{ai}^i B_{b1}^1 B_{b2}^2 ...... B_{bj}^j = \sum_{i,j} A_{m_i}^i B_{n_j}^j \qquad (4)$$

where $A_{a_i}^i,$ $B_{b_j}^j$ show the different constituent elements or different sites of the same element in the crystal formula, and a_i, b_j are the number of the corresponding elements. $N(B^j - A^i)$ is the number of B^j ions in the coordination group of a A^i ion, and N_{CA^i} represents the nearest coordination number of the A^i ion. Therefore, the complex crystal is decomposed into the sum of diverse binary crystals like $A_{m_i}^i, B_{n_j}^j$. For any binary $A_m B_n$, charge Q_A is the normal valence of the cation A, and Q_B is that obtained from $Q_B = \dfrac{m Q_A}{n}$.

According to PV[5] and Levine's theory,[4] the total macroscopic linear susceptibility χ of crystals from the various types of bonds can be represented by the

following equation:

$$\chi = \sum_{\mu} F^{\mu} \chi^{\mu} = \sum_{\mu} N_b^{\mu} \chi_b^{\mu} \tag{5}$$

$$\epsilon^{\mu} = 1 + 4\pi \chi^{\mu} \tag{6}$$

Where ϵ is the crystal dielectric constant, obtained from the index of refraction n ($\epsilon = n^2$). ϵ^{μ} is the dielectric constant of a μ type chemical bond, F^{μ} is the fraction of bonds of type μ composing the actual crystal, χ_b^{μ} is the susceptibility of a single bond of type μ, and N_b^{μ} is the number of bonds per cubic centimeter. χ^{μ} is the total macroscopic susceptibility which a crystal composed entirely of bonds of type μ would have, which can be shown as:

$$\chi^{\mu} = (4\pi)^{-1} \left(\hbar \Omega_p^{\mu} \right)^2 / (E_g^{\mu})^2 \tag{7}$$

Where E_g^{μ} is the average energy gap for μ type bonds (in eV), Ω_p^{μ} is the plasma frequency obtained from the number of valence electrons of type μ per cubic centimeter N_e^{μ}, using the following equation:

$$\left(\Omega_p^{\mu} \right)^2 = (4\pi (N_e^{\mu})^* e^2 / m) D^{\mu} A^{\mu} \tag{8}$$

Where D^{μ} and A^{μ} are correction factors, their expressions are:

$$D^{\mu}(A,B) = \Delta_A^{\mu} \Delta_B^{\mu} - \left(\delta_A^{\mu} \delta_B^{\mu} - 1 \right) [\left(Z_A^{\mu} \right)^* - \left(Z_B^{\mu} \right)^*]^2 \tag{9}$$

$$A^{\mu} = 1 - \left(\frac{E_g^{\mu}}{4E_F^{\mu}} \right) + (\frac{E_g^{\mu}}{4E_F^{\mu}})^2 / 3 \tag{10}$$

Where $(Z_A^{\mu})^*$ and $(Z_B^{\mu})^*$ are the numbers of effective valence electrons on the A and B atoms of the μ bond, Δ and δ are the periodic dependent constants[4]. The Fermi

energy E_F^μ (in eV) is given in terms of the Fermi wave vector E_F^μ by

$$E_F^\mu = (\hbar K_F^\mu)^2/2m \quad (11)$$

$$(K_F^\mu)^3 = 3\pi^2 (N_e^\mu)^* \quad (12)$$

Here, $(N_e^\mu)^*$ is the effective valence electron density for the μ bond per cubic centimeter and it is given by:

$$(N_e^\mu)^* = (n_e^\mu)^*/v_b^\mu \quad (13)$$

$$(n_e^\mu)^* = \frac{(Z_A^\mu)^*}{N_{CA}^\mu} + \frac{(Z_B^\mu)^*}{N_{CB}^\mu} \quad (14)$$

$$v_b^\mu = (d_\mu)^3 / \sum_\nu (d_\nu)^3 N_b^\nu \quad (15)$$

Where, $(n_e^\mu)^*$ is the number of effective valence electrons per μ bond. The bond volume v_b^μ (Å³) for the bonds of type μ is proportional to $(d_\mu)^3$, where d_μ is the bond distance (Å). N_b^ν is the number of bonds of type ν per cubic centimeter. The average energy gap E_g^μ (eV) can be separated into homopolar energy E_h^μ (eV) and heteropolar energy C^μ (eV) as shown in the equation below:

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \quad (16)$$

The covalency of any μ type bonds is defined as:

$$f_c^\mu = (E_h^\mu)^2/(E_g^\mu)^2 \quad (17)$$

Where

$$E_h^\mu = 39.74/(d_\mu)^{2.48} \quad (18)$$

$$C^{\mu} = 14.4 b^{\mu} \exp\left(-k_s^{\mu} * r_o^{\mu}\right)\left[\left(Z_A^{\mu}\right)^* - \left(\frac{n}{m}\right)\left(Z_B^{\mu}\right)^*\right]/r_o^{\mu} \quad (n > m) \text{ (eV)} \quad (19)$$

$$C^{\mu} = 14.4 b^{\mu} \exp\left(-k_s^{\mu} * r_o^{\mu}\right)\left[\left(\frac{m}{n}\right)\left(Z_A^{\mu}\right)^* - \left(Z_B^{\mu}\right)^*\right]/r_o^{\mu} \quad (n \leq m) \text{ (eV)} \quad (20)$$

With

$$r_o^{\mu} = d_{\mu}/2 \quad (21)$$

$$k_s^{\mu} = \left(\frac{4k_F^{\mu}}{\pi \alpha_B}\right)^{1/2} \quad (22)$$

Here, k_s^{μ} is the Thomas-Fermis screening wavenumber of valence electrons and α_B is the Bohr radius. b^{μ} is shown in the following equation:

$$b^{\mu} = \beta(N_C^{\mu})^2 \quad (23)$$

$$N_C^{\mu} = mN_{CA}^{\mu}/(m + n) + n\, N_{CB}^{\mu}/(m + n) \quad (24)$$

Where b^{μ} depends on the crystal structure.

Once the dielectric constant of the crystal is known, the value of β can be deduced from the above equations. When the dielectric constant is unknown, it may also be estimated by using the β value of its isostructural crystals. The environmental factor designated by the symbol he can be expressed as:[6, 7]

$$h_e = \left(\sum_{\mu} f_c^{\mu} \alpha_b^{\mu} Q_B^{\mu 2}\right)^{1/2} \quad (25)$$

Where Q_B^{μ} stands for the presented charge of the nearest anion in the chemical bond, and α_b^{μ} is the polarizability of the chemical bond volume in the μ type of chemical

bonds.

For the chemical bond of type μ, the polarizable coefficient α_o^μ can be obtained from the Lorentz-Lorenz equation:

$$\frac{\epsilon^\mu - 1}{\epsilon^\mu - 2} = (4\pi/3)\alpha_o^\mu \tag{26}$$

Hence, the polarizability of the chemical bond volume (Å^3) is given by

$$\alpha_b^\mu = \alpha_o^\mu v_b^\mu \tag{27}$$

By zhang's analysis, the charge transition energy (E_{ct}) could be obtained by the following empirical formula:

$$E_{ct} = A + Be^{-kh_e} \tag{28}$$

Where A=2.804, B=6.924, and k=1.256 for the Eu^{3+} ion. These constants only relate to the type of rare earth ion.

Reference

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